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RESEARCH LETTER

Modification of chitosan films with environmentally benign reagents for increased water resistance

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Chitosan is a non-toxic, renewable, abundant natural material with excellent film-forming properties. It is shown here that water absorption by chitosan films can be decreased by chemical modification with the bio-based reagents citric acid and glycerol. Infrared spectroscopy showed that citric acid reacted with chitosan amine groups to form an acyclic amide structure. Glycerol imparted flexibility and water repellency to the films. When soaked in water for six hours, a chitosan–citric acid–glycerol (1:1:9) film absorbed 44% water by weight after initial exposure and remained unchanged for the duration of the experiment. In comparison, a pure chitosan membrane initially absorbed 70% water and gradually increased to 96%. After soaking, the modified film swelled by only 11% compared to 42% for pure chitosan. Similar results were observed for water contact angle with the film surfaces. For the modified film, change in contact angle over time could be attributed solely to evaporation, whereas the pure chitosan film absorbed the droplets. These results show that the properties of chitosan can be improved using environmentally benign reagents in accordance with green chemistry principles.

Keywords: chitosan; citric acid; glycerol; polymer films; water absorption; renewable resources

Introduction

Synthetic polymers account for a significant fraction of annual petroleum consumption (approximately 5%) and product value (1). Increasing pressures on supplies of fossil fuels, toxicity of commonly used monomers, and polymer non-biodegradability are all concerns that may be addressed by invention of new polymer materials based on biological feedstocks (2). Complementing and combining new polymer classes with the petroleum-based polymers will be important both scientifically and in the development of new performance, new properties, and continued market acceptance. Recently, the National Research Council of the National Academies outlined eight “Grand Challenges” that must be addressed in this century to achieve sustainability in the chemical enterprise. One of the eight challenges is deriving chemical feedstocks from renewable resources. Among the research needs identified is development of “fundamentally new compounds from platforms such as lignin, sugar, or cellulose” (3,4).

Among the most abundant biopolymers is chitin (Figure 1), a structural component of crustacean and insect exoskeletons as well as fungal cell walls. Chitin and its *N*-deacetylated derivative, chitosan, are non-toxic and biodegradable. Chitosan is found naturally

in certain fungi or can be manufactured by chemical processing of chitin (5). Because of its more favorable solubility properties, it has been developed more than chitin as a platform for new materials. The many opportunities for derivation, either at the amine or hydroxyl positions, have allowed researchers to devise new bio-based polymers with a wide range of functional groups and mechanical properties (6). Chitosan and its derivatives have already found applications as ingredients in cosmetics and personal care products, as adsorbents for waste water treatment, controlled-release agents, artificial human tissue, and biodegradable food packaging (5,7).

Chitosan has excellent film-forming properties but its poor water resistance limits its utility in some applications. Chemical modifications are possible to improve the water repellency of the natural material. For example, hydrophobic chitosan films have been demonstrated previously by reaction with perfluorinated acid derivatives (8). The persistence, bioaccumulation, and endocrine-disrupting potential of perfluorinated chemicals has driven the call for alternatives (9). Here we report a facile preparation of chitosan membranes with increased water repellency, taking full advantage of renewable resources that might otherwise be regarded as waste materials. This

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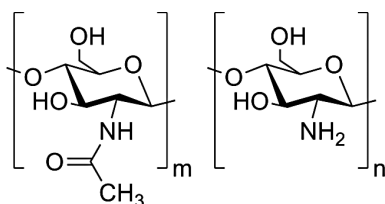


Figure 1. Chitin and chitosan. These are random copolymers of 2-acetamido-2-deoxy- β -D-glucose and 2-amino-2-deoxy- β -D-glucose. Chitin is usually $\sim 90\%$ acetylated; “chitosan” refers to polymers that are less than 50% acetylated.

approach can expand the potential value and application areas for the bio-based materials used (10). It is shown that chitosan reacts with citric acid, forming an amide linkage. Citric acid, an intermediate in human metabolism, is a renewable feedstock that is produced commercially by fermentation of sucrose or glucose, from sources such as sweet potato (11,12) or black liquor from wood pulping. The reaction between citric acid and chitosan has been previously reported but the properties and characteristics of the material produced in that study are significantly different from those reported here (13). Introduction of glycerol to the chitosan–citric acid films imparts flexibility. Glycerol is a known plasticizer of chitosan films and has also been used to prepare biodegradable citric acid-based polyesters (14). This paper surveys the effects of varying ratios of citric acid and glycerol on chitosan chemical structure (as measured by infrared spectroscopy) and water repellency (as measured by change in water uptake, dimensional stability, and contact angle over time).

Results and discussion

Effect of citric acid and glycerol on chitosan membrane structure

Chitosan, citric acid, and glycerol in the ratios specified in Table 1 were allowed to react under dehydrating conditions. Infrared spectroscopy via attenuated total reflectance was used to characterize the resulting films. The cellulose filter papers used to facilitate removal of films from their petri dishes were inert to reaction under the experimental conditions, as evidenced by IR spectra of control filter paper–citric acid and filter paper–chitosan samples.

The IR spectra of the “A” series (chitosan and citric acid without glycerol) showed changes as the proportion of citric acid increases (Figure 2). The peak in the range $2500\text{--}3500\text{ cm}^{-1}$ became broader due to the OH groups in citric acid. Similarly, the chitosan C–O absorption at 1182 cm^{-1} became broader due to the contributions of citric acid C–O

Table 1. Chitosan–citric acid–glycerol films prepared in different ratios.

Sample name	Chitosan	Citric acid	Glycerol
A1	1	1	0
A2	3	1	0
A3	1	3	0
B1	1	1	1
B2	3	1	1
B3	1	3	1
C1	1	1	3
C2	3	1	3
C3	1	3	3
D1	1	1	9
D2	3	1	9
D3	1	3	9

bonds. The remaining spectral changes can be attributed to formation of an amide bond between citric acid and the chitosan amine group. Both acyclic and cyclic amides are theoretically possible (Figure 3).

A C=O stretching absorption appeared at 1708 cm^{-1} . According to the literature pure citric acid exhibits two C=O peaks, one around 1750 cm^{-1} and the other around 1700 cm^{-1} , corresponding to free and hydrogen-bonded carboxylic acid groups (11). After reaction with chitosan, the peak at 1750 cm^{-1} disappeared and there were no new peaks in the 1730 cm^{-1} region indicating that esterification did not occur. A literature report on citric acid amides found that an acyclic amide showed characteristic C=O absorption near 1625 cm^{-1} , whereas the cyclic amide analog appeared at 1770 cm^{-1} (15). The absence of peaks in the 1770 cm^{-1} region of the chitosan–citric acid spectrum rules out the cyclic structure. Chitosan shows NH_2 bending vibrations at 1648 cm^{-1} and 1581 cm^{-1} . These peaks should overlap with acyclic amide I and II absorptions. Indeed, it can be seen that with increasing citric acid, these peaks shifted to lower wavenumbers and became broader. Further evidence for disruption of the original structure of chitosan is broadening of peaks in the $560\text{--}670\text{ cm}^{-1}$ region. Mima et al. have shown that these peaks are sharpest for 99% deacetylated chitosan and that they gradually disappear with increasing acetylation (i.e. amide formation) (16). Thus, it is concluded that under the conditions of these experiments, chitosan and citric acid reacted to form an acyclic amide. This is analogous to reports of wool–citric acid derivatives prepared by a similar technique (17).

Introduction of glycerol to the film-forming reaction did not significantly impact the infrared spectra (series B, C, and D). There were no new peaks in the ester C=O absorption region, indicating that glycerol and citric acid did not form esters under

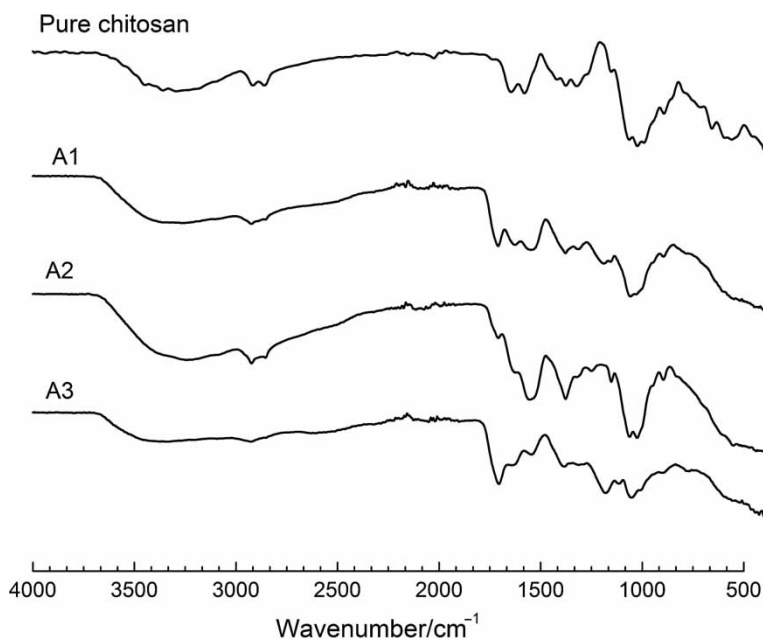


Figure 2. Infrared spectra (% transmittance) of chitosan–citric acid films. The axes have been offset for clarity.

the conditions used. When a reaction was attempted with only glycerol and citric acid, with no chitosan, no film was formed and the resulting material was completely water-soluble. This suggests that the role of glycerol in the chitosan–citric acid system was as a plasticizer and it was observed that with increasing glycerol content the films became more flexible. Series A was extremely brittle and cracked spontaneously upon cooling at the end of the reaction; series D was highly flexible.

Effect of citric acid and glycerol on chitosan water absorption

Water absorption was determined by measuring the mass of pure chitosan and film D1 before and after soaking in water (Figure 4). Water uptake for both films was most rapid in the first three minutes of exposure. The water content of the modified film did not change after that point. After six hours, the water absorption by mass was 96% for pure chitosan, compared to 44% for film D1. Similar results were seen in thickness measurements. The thickness of the

pure chitosan film increased by 42%, whereas film D1 increased by only 11%.

Water contact angles were recorded to measure hydrophobicity and absorption of water over time (an example photograph is shown in Figure 5). Poly(tetrafluoroethylene) (PTFE) tape was included as a model hydrophobic material (18). Among the chitosan–citric acid films (series A–D) the average initial contact angle is about 65°, with slightly higher results seen for C1 and the D series (approximately 75°) (Figure 6). Since the infrared spectra do not show significant changes in the A–D series, it is not surprising that the contact angles are relatively constant. In the literature, the contact angle of water on pure chitosan films has been reported in the range 76–104° depending on the study (19–21). However, a single contact angle measurement cannot reflect how quickly water is absorbed by chitosan.

In this study, PTFE tape was used as a non-water-absorbing control to show change in contact angle over time due to evaporation. Figure 7 shows the results for PTFE, chitosan–citric acid–glycerol films, and pure chitosan. For all samples the initial decrease in contact angle over time was a linear response. The slopes of linear fits for A1, B1, and C1 were steeper than that of PTFE, indicating that in addition to evaporation of water, these samples absorbed water from the film surface (Table 2). When the highest amount of glycerol was used (D1) the initial contact angle was higher and the rate of change over time was identical to that of PTFE, indicating significantly

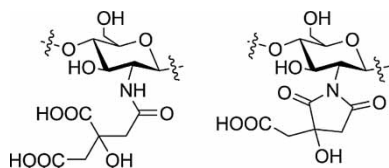


Figure 3. Possible amide structures from reaction of citric acid with chitosan.

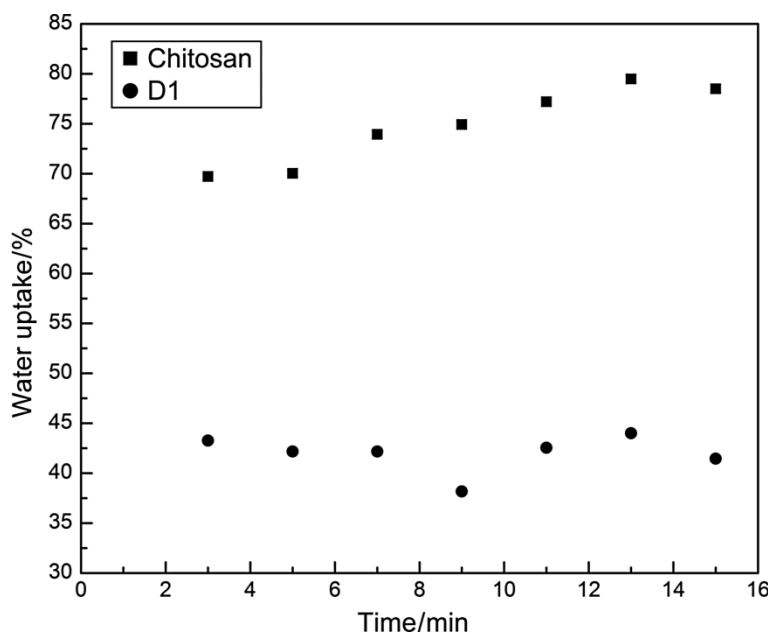


Figure 4. Water uptake over time by pure chitosan and modified chitosan films.

reduced water absorption in agreement with the changes in mass and thickness discussed above.

The plasticizing effect of glycerol may have resulted in a smoother, less porous film. As mentioned above, the A series was extremely brittle and prone to cracking. Similarly, the B and C series may have also suffered from structural defects. The roughness of a surface is known to affect contact angle (22). Further experiments will be conducted to measure the morphology of the chitosan–citric acid films as a function of glycerol content.

Experimental

Materials

Chitosan was purchased from TCI America (88.2% deacetylated). Glycerol (electrophoresis grade, >99%)

was purchased from Sigma, citric acid (99+%) was purchased from Alfa Aesar and glacial acetic acid was purchased from J.T. Baker. All chemicals were used as received. Deionized water was used in all experiments.

Film preparation

Chitosan–citric acid films were prepared as follows: chitosan flakes were dissolved in 1% acetic acid to which was added the desired amounts of citric acid and glycerol (exact amounts are shown in Table 1). To produce films of uniform thickness, the total weight of dissolved species in each experiment was 1 g. After complete dissolution of the ingredients,

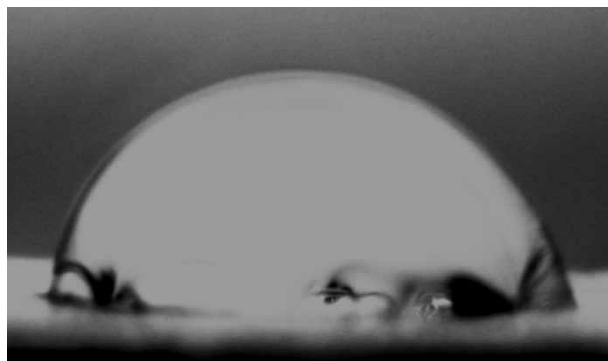


Figure 5. Surface profile of a water droplet on a chitosan–citric acid–glycerol film surface (sample D1, prepared with reactants in the ratio of 1:1:9). The contact angle is 79°.

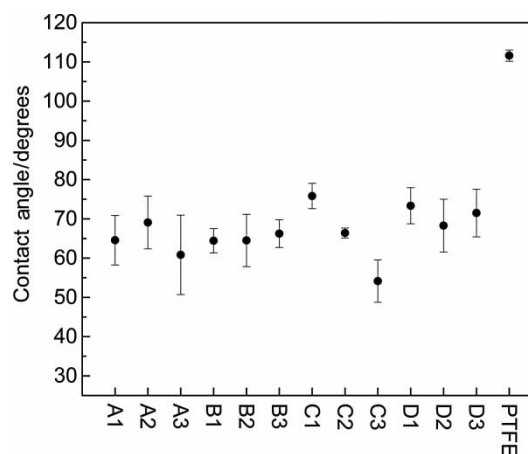


Figure 6. Initial water contact angles measured for chitosan–citric acid and PTFE films with varying amounts of glycerol (series A–D).

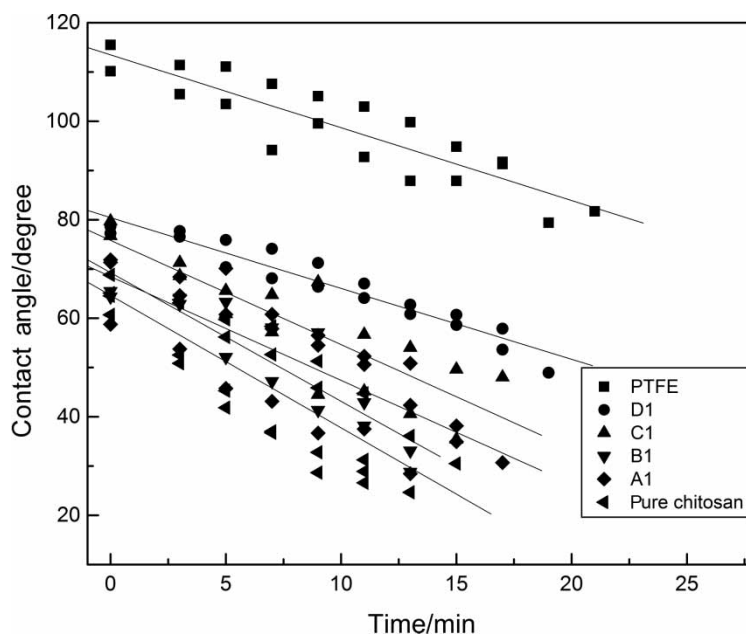


Figure 7. Change in contact angle with time.

each solution was cast in a petri dish containing one filter paper circle (cellulose, 7 cm diameter, Whatman No. 1, cat no. 1001-070). The Petri dishes were dried overnight in a convection oven at 60°C to evaporate acetic acid solution. The temperature was then increased to 110°C for 6 hours. The Petri dishes were briefly submerged in deionized water to facilitate removal of the films, which were then air-dried.

Infrared measurements

Infrared spectra were recorded using a Nicolet 6700 FT-IR spectrometer equipped with a diamond ATR accessory. Spectra were acquired in the range 500–4000 cm^{-1} .

3.4 Swelling and water uptake behavior

Thickness was measured with a micrometer (Marathon Watch Company CO 030025, accuracy 0.002 mm). Films of identical starting thickness (0.170–0.180 mm)

were cut to 1 cm by 2 cm dimensions, then soaked in water for 6 hours. Measurements were taken in five places before and after the wetting process. Prior to measuring the final thickness, water on the surface of the films was blotted with filter paper. Percent water uptake (w/w) was calculated from measurements of mass after soaking in water for various periods of time.

Contact angle measurements

The water contact angle of the films was measured using VCA OPTIMA equipment (AST Products, Boston, MA). Each sample was measured three times using the sessile drop method immediately after wetting of the surface. Droplets of distilled water were examined at five different sites on each slide sample. All measurements were performed at room temperature.

Conclusions

This study has shown that modified chitosan films with increased water resistance can be prepared entirely from non-toxic, renewable feedstocks. Citric acid reacted to form amide linkages, disrupting the original chitosan structure. The addition of glycerol had a plasticizing effect which was critical to reducing water absorption by the films. Further development of this material will promote the use of currently underutilized, environmentally benign starting materials in applications such as packaging, coatings, and

Table 2. Change in contact angle with time: slope of linear fits.

Samples	Slope of linear fit (Figure 6)
PTFE	-1.478 ± 0.172
D1	-1.439 ± 0.100
C1	-2.117 ± 0.316
B1	-2.612 ± 0.359
A1	-2.029 ± 0.457
Pure chitosan	-2.689 ± 0.341

drug-release matrices where increased water resistance is desirable.

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